

N94-16331

# EVAPORATION KINETICS OF $\text{Mg}_2\text{SiO}_4$ CRYSTALS AND MELTS FROM MOLECULAR DYNAMICS SIMULATIONS;

J. D. Kubicki and E. M. Stolper, Division of Geological and Planetary Sciences, California Institute of Technology, 170-25 Pasadena, CA 91125

**Abstract.** Computer simulations based on the molecular dynamics (MD) technique have been used to study the mechanisms and kinetics of free evaporation from crystalline and molten forsterite (i. e.,  $\text{Mg}_2\text{SiO}_4$ ) on an atomic level. The interatomic potential employed for these simulations reproduces the energetics of bonding in forsterite and in gas-phase  $\text{MgO}$  and  $\text{SiO}_2$  reasonably accurately. Results of the simulation include predicted evaporation rates, diffusion rates, and reaction mechanisms for  $\text{Mg}_2\text{SiO}_4(\text{s or l}) \rightarrow 2\text{Mg}(\text{g}) + 2\text{O}(\text{g}) + \text{SiO}_2(\text{g})$ .

**Introduction.** Hashimoto [1] showed that evaporation and condensation kinetics played a role in the cosmochemistry of the early solar nebula. Davis et al. [2] demonstrated based on the results of evaporation experiments on forsterite crystals and melt that the so-called FUN CAI's (fractionated and unknown nuclear effect; calcium-, aluminum-rich refractory inclusions) in carbonaceous chondrites could have obtained anomalous isotopic signatures from kinetic isotope effects during non-equilibrium evaporation. In their experiments, however, isotope fractionations were significant only for molten  $\text{Mg}_2\text{SiO}_4$  and not crystalline forsterite. They explained this as due to the fact that the rate of evaporation from the solid is much faster than the rate of diffusion, so no isotopic fractionation is possible. In contrast, diffusion and evaporation rates operate on similar time scales in the molten phase, so a significant vapor-liquid isotopic fractionation occurs because light isotopes from the interior of the melt diffuse to the surface as fast as they are evaporated. This study was conducted to investigate possible mechanisms of evaporation from forsterite crystals and melts. Such simulations can lead to insights into the main evaporating species (i.e.,  $\text{SiO}(\text{g})$  vs.  $\text{SiO}_2(\text{g})$ ) and into the factors influencing the magnitude of kinetic isotope effects accompanying evaporation.

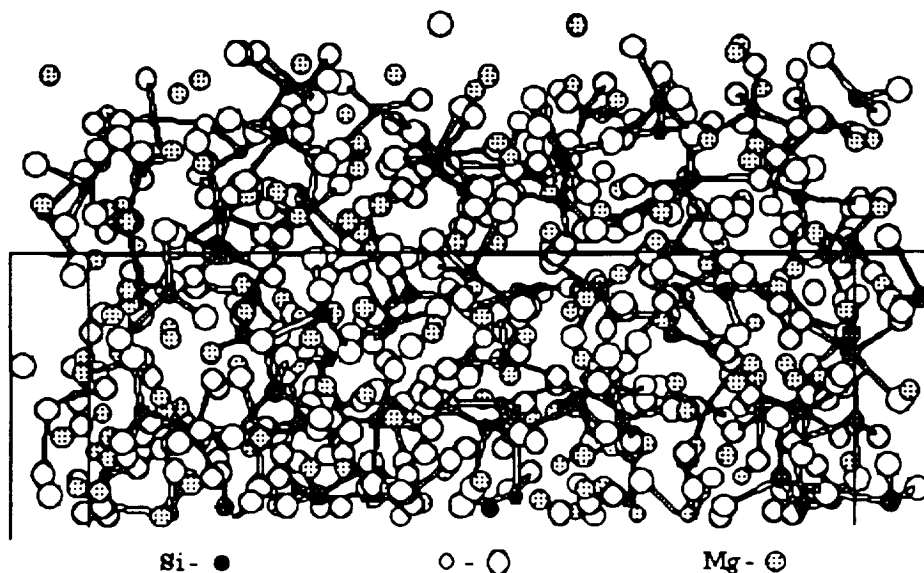


Figure 1 - Edge view of forsterite crystal evaporating. Lines denote boundaries of MD cell.

**Methodology.** MD simulations calculate the motion of particles in an atomic system with Newton's equations of motion employed over small time increments, usually  $10^{-15}$  s. The extremely small time steps are required to conserve the energy of the system but this causes the real time duration of the simulation to be short (i. e.,  $10^{-10}$  to  $10^{-12}$  seconds). Structural, thermodynamic, and kinetic properties of the system can be calculated with the MD technique. (For a review, see [3, 4]). The MD system in this study consisted of 1680 atoms (240  $\text{Mg}_2\text{SiO}_4$  formula units) with initial crystal positions determined from the experimental crystal coordinates.  $\text{Mg}_2\text{SiO}_4$  melts were generated from the simulations of [5] with 1280 atoms in the MD cell. Two-dimensional periodic boundary conditions were employed along the a- and b-axes, approximating an infinite layer with a thickness along the c-axis of 24 Å in the crystalline phase (Fig. 1) and 16 Å in the molten phase (Fig. 2). The potential of Leinenweber and Navrotsky [6] was used to model the interactions of  $\text{Si}^{4+}$ ,  $\text{Mg}^{2+}$ , and  $\text{O}^{2-}$  ions within the evaporating forsterite. We chose this potential because it accurately reproduces mineral structures in the Mg - Si - O system [6], and also

## EVAPORATION OF FORSTERITE FROM MD SIMULATIONS: J.D. Kubicki and E.M. Stolper

does an accurate job of fitting the energetics of neutral gas phase molecules [7]. Evaporation rates were determined from simulations at 3000, 4000 and 5000 K in the crystalline phase and 4000, 5000, and 6000 K in the molten phase. The positions of all particles are known as a function of time, so the evaporation rate is the number of ions leaving the mineral surface per unit time per unit surface area. Atomic masses are read in as part of the input data set; hence, it is possible to isotopically "dope" the simulated mineral with  $^{18}\text{O}$ ,  $^{26}\text{Mg}$ , and  $^{30}\text{Si}$ . Relative rates of evaporation versus diffusion (calculated with the Einstein equation) can be compared in the crystalline and melt phases.

**Results and Discussion.** Due to the short durations of the MD simulations, the evaporation and diffusion rates are most accurately determined at temperatures much higher than normally employed in the laboratory. However, the short time duration also allows crystalline systems to be studied at temperatures far above the melting point because the system remains crystalline metastably [8]. Evaporation rates predicted from the simulations are on the order of 1 to 10 mol/cm<sup>2</sup>/sec at 3000 to 6000 K in both crystalline and molten  $\text{Mg}_2\text{SiO}_4$  similar to values obtained from extrapolation of the experimental data [1]. Evaporation from crystals occurs more rapidly than from melts at the same temperature in these simulations, but diffusion is more rapid in the melt phase. This is also evidenced in the melt simulation by mixing of isotopes initially placed in separate regions of the cell (Fig. 2); whereas, in the simulations of crystalline  $\text{Mg}_2\text{SiO}_4$ , the isotopes do not mix significantly from one crystal plane to the next (Fig. 1). These results are consistent with Hashimoto's [1] interpretation of the experimental data.

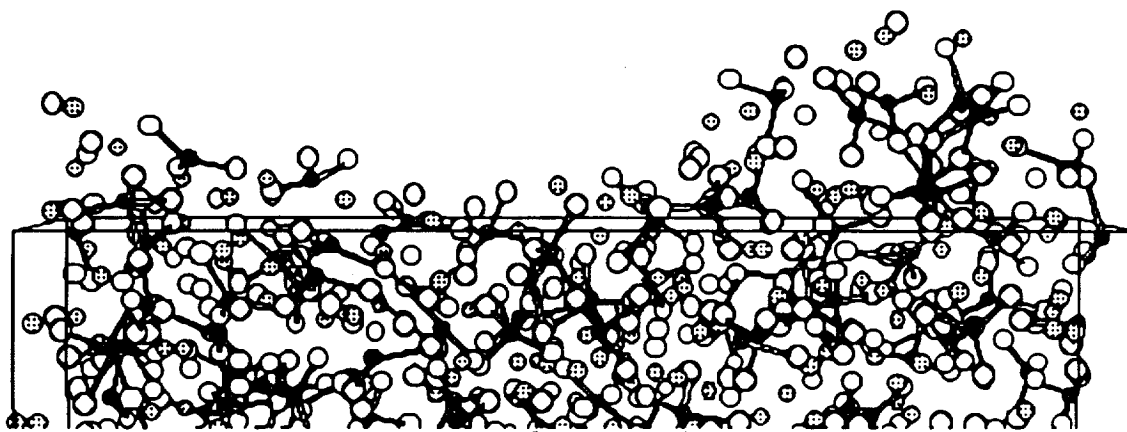


Figure 2 - Surface of molten  $\text{Mg}_2\text{SiO}_4$  shows  $\text{Mg}^{2+}$  and  $[\text{SiO}_4]^{4-}$  anions evaporating and diffusion in the melt as heavy isotopes ( $^{18}\text{O}$ ,  $^{26}\text{Mg}$ , and  $^{30}\text{Si}$ ), initially in the right-hand side of the cell, mix with light isotopes on the left. (Key in Fig. 1).

The reaction mechanism predicted in the MD simulations is somewhat different from the experimental interpretation, however. Although the ionic nature of the interatomic potential may be somewhat inaccurate for modelling neutral atoms, the species leaving the surface are dominated by  $\text{Mg}^{2+}$  and  $[\text{SiO}_4]^{4-}$  ions rather than Mg and O atoms and  $\text{SiO}_2$  molecules. Such speciation may contribute to the larger isotopic fractionation of Mg during evaporation of  $\text{Mg}_2\text{SiO}_4$  melts compared to O and Si [2] because the larger  $[\text{SiO}_4]^{4-}$  anion will be less affected by small mass differences due to isotopic substitutions compared to the atoms and molecular  $\text{SiO}_2$ . Gas-phase reactions could subsequently lead to conversion of  $2\text{Mg}^{2+} + [\text{SiO}_4]^{4-} \rightarrow \text{SiO}_2 + 2\text{O} + 2\text{Mg}$ .

**References** [1] Hashimoto A, 1990, *Nature*, **347**, 53-55. [2] Davis AM, A Hashimoto, RN Clayton, and TK Mayeda, 1990, *Nature*, **347**, 655-658. [3] Kubicki JD and AC Lasaga, 1990, *Advances in Physical Geochemistry*, Vol. 8, Springer-Verlag, New York, pp. 1-50. [4] Ciccotti G, D. Frenkel, and IR MacDonald, eds, 1987, *Simulation of Liquids and Solids*, North-Holland, Amsterdam. [5] Kubicki, JD and AC Lasaga, 1991, *Phys. Chem. Min.* **17**, 661-673. [6] Leinenweber K and A Navrotsky, 1988, *Phys. Chem. Min.* **15**, 588-596. [7] Kubicki JD, 1991, *Eos, Trans. Am. Geophys. Union*, **72**, 144. [8] GD Price and Matsui M and 1991, *Nature*, **351**, 735-737.